John Sherwell[1], Mark Garrison[2], Tom Wickstrom[2], Anand Yegnan[2],
Mark Castro[3], Chris Moore[3]
[1]Maryland Department of Natural Resources, Annapolis, MD
[2]Environmental Resources Management, Exton, PA
[3]University of Maryland Center for Environmental Science, Frostburg, MD

Progress Towards Evaluating and Modeling Long-Term Patterns of Speciated Mercury Concentrations in Maryland Using CALPUFF

NADP 2007
Wet and Dry Deposition Measurements:
Do We Have the Total Picture?

Boulder, Colorado
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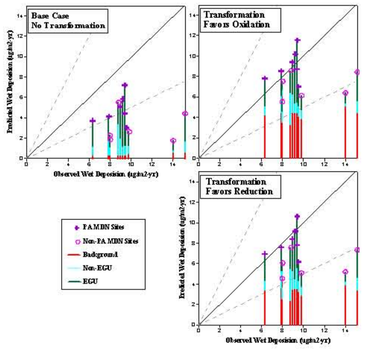
Starting Point: Initial Development and Evaluation of CALPUFF with Mercury Algorithms

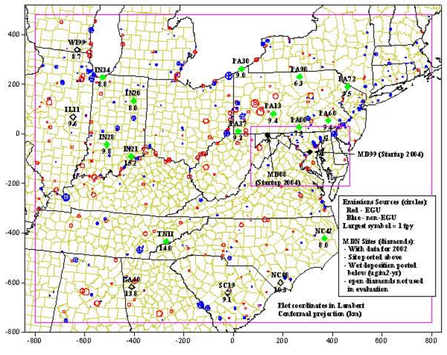
Mercury Adaptations Required for a Lagrangian Puff Model

- CALPUFF is a publicly available Lagrangian Puff model well-suited for identifying source contributions (http://www.epa.gov/scram001/dispersion_prefrec.htm#calpuff)
- Mercury transformation mechanisms within the grid models REMSAD and CAMx were examined and used to build a box model to investigate and adapt for inclusion in CALPUFF.
- Transformation rates were adapted to create two options within CALPUFF: one favoring oxidation from GEM to RGM and one favoring reduction of RGM to GEM.
- Defining concentrations of reacting species was necessary to drive the transformation chemistry; some examples of how this is done:
  - Ozone concentrations: existing CALPUFF scheme used (surface measurements interpolated to grid cell locations)
  - Radical concentrations: Seasonal, climatic values
  - Chlorine concentrations: Constant values, different for land and ocean, zero aloft (similar to REMSAD, CAMx)
- The current version of CALPUFF with mercury chemistry has a complete dry transformation scheme, while the aqueous transformations are highly parameterized. Work has also been done with a parameterized version of the dry transformation mechanisms.

Model Evaluation – Weekly Wet Deposition



Mercury Sources and MDN Locations



Study Overview and Objectives

The Sad Story of Model Evaluation

- Regional scale model evaluations are limited by the availability of complete emissions inventories. Typically the National Emissions Inventory (NEI) is updated every three years (e.g. 2002, 2005) and it takes several years for the U.S. EPA to update (although with mercury, EGU can be estimated by utilizing operational data contained in the continuous emissions monitor (CEM) hourly files for larger units).
- Limitations also exist with respect to the availability of recent meteorological data – both measurements and modeled profiles (such as those produced with the use of MM5).
- Measurements on a broad scale, over a long time period, have historically been limited to weekly wet deposition measurements. Although the number of measurement locations recording semi-continuous, speciated concentrations have increased recently, the problem of concurrent meteorology and inventory information limits the degree to which evaluations can be carried out.
- Ultimately the usefulness of a model to estimate atmospheric mercury impacts depends on the model's ability to estimate deposition, wet and dry. Actual measurements of dry deposition are difficult and scarce, so model evaluations are limited to considering concentrations and wet deposition.

Overall Objectives

- Develop a Maryland-focused model to investigate Hg deposition within the State
- Utilize a readily available modeling platform that can be adapted to estimate Hg concentrations and deposition with an emphasis on impacts on a local to Maryland-wide scale
- Develop algorithms to be as consistent as possible with large-scale grid models
- Evaluate model performance, assess model strengths and limitations to be clearly articulated in model applications
- Develop sufficient geographic resolution to enable evaluation of Hg deposition for specific watersheds and water bodies
- Establish benchmark mercury loading contributions of Maryland and regional sources (including different source sectors) to mercury deposition throughout Maryland and within Maryland water bodies and watersheds of interest. Identify source contributions in enough detail to estimate relative roles of in-state, out-of-state, and global sources, and the relative roles of EGU and non-EGU sources
- Utilize modeling platform to assist in evaluating the effects of mercury emissions reductions due to state and federal programs

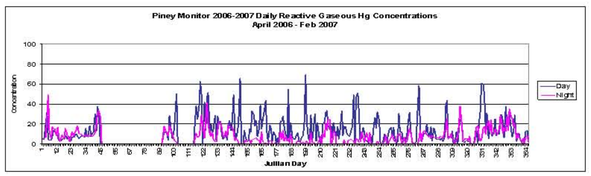
Accomplishments to-date

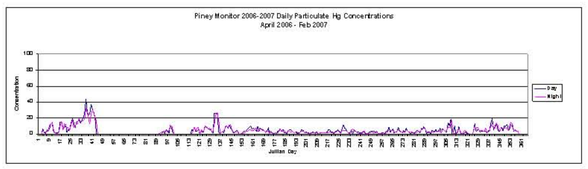
- Developed a version of the publicly-available CALPUFF model that incorporates mercury transformation and deposition algorithms
- Developed a mercury emissions inventory for 2002 based on National Emissions Inventory (NEI) data for 1999 and 2002
- Prepared three-dimensional meteorological inputs for 2002 based on MM5 data produced by the University of Maryland. Extent of meteorological and emissions domain shown on the map.
- Conducted limited model evaluations comparing predicted weekly wet deposition estimates with measurements taken at MDN sites for 2002;
- Evaluation Summary:
  - Model predicted better for locations close to Maryland and the center of the domain;
  - Model underestimated deposition on edges of domain, possibly due to lack of input from nearby upwind source;
  - Generally good agreement on an annual average basis; seasonal patterns are similar
- Conducted modeling covering the State of Maryland to investigate source contributions to mercury loading on Maryland water bodies
- Extended modeling to cover the Chesapeake Bay Watershed
- Model evaluation of aggregated weekly wet deposition only provides limited confidence in model performance

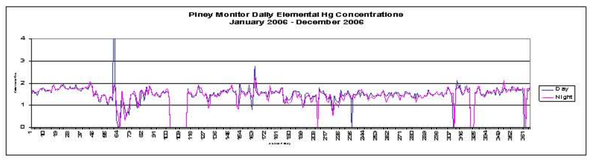
Present Study

- PPRP has deployed a Tekran ambient speciation unit at a site in Western Maryland, at Piney Reservoir (MDN site MD08 – see map), operated by the UMd CES. The Maryland Department of the Environment measures numerous other gaseous pollutants and meteorological parameters at the site.
- The Tekran instrument measures semi-continuous speciated mercury concentrations. Preliminary analysis of recent data (April 2006 to July 2007) was conducted to investigate whether any dominant patterns can be detected (diurnal, seasonal, nature of short-term peaks).
- Modeling was updated by scaling electrical generating unit (EGU) emissions to calendar year 2006 based on recorded fuel usage for the base year (1999) and 2006; adjustments were also made to EGU emissions for plants that have installed scrubbers since the base year.
- Meteorological data was updated to three full calendar years (2001-2003) based on MM5 data produced by the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) organization in conjunction with their work on Regional Haze. Work is progressing on developing a full ten year meteorological data set
- The focus of the present study is to further previous evaluations of wet deposition by examining dominant patterns of measured and modeled concentration time series, and to evaluate numerical consistency.

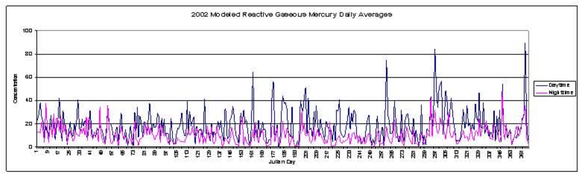
Measured Data – Piney Reservoir, MD

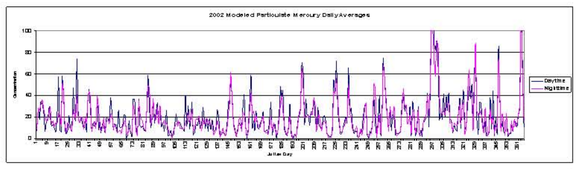


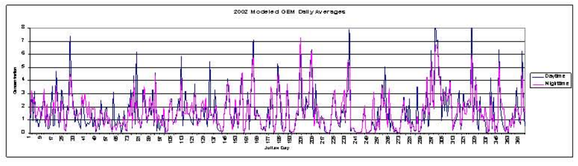




Modeled Data – Piney Reservoir, MD

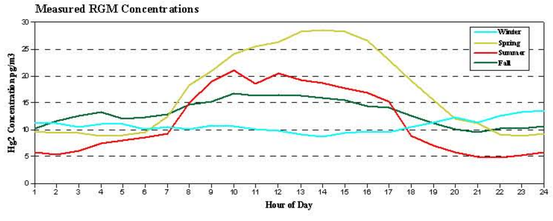




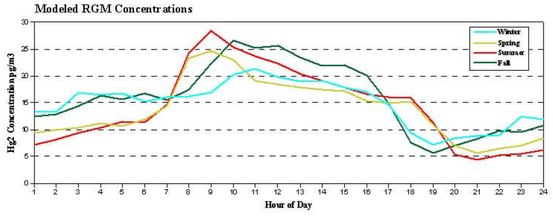


Time Series were created for each species showing the average concentration at night and during the day

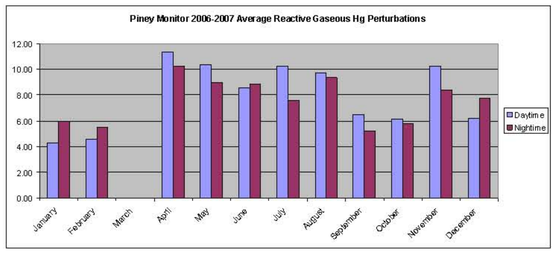
Measured RGM Concentrations

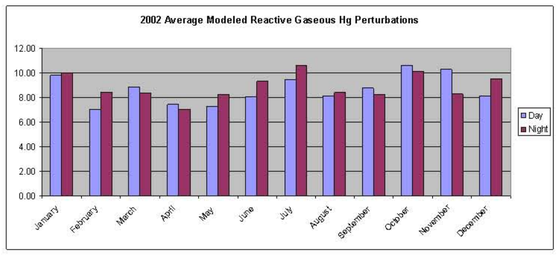


Modeled RGM Concentrations



Diurnal plots are shown that illustrate measured and modeled patterns of RGM concentrations, by season





Monthly "perturbation" plots were created by calculating the average difference between each observation and the daily average for each month

Conclusions

An evaluation of measured and model-predicted speciated mercury concentrations at the Piney Reservoir site in Western Maryland (MD08) revealed some encouraging comparisons, while at the same time pointing out areas where model improvements need to be made. For RGM, the numerical values, diurnal, and seasonal patterns seem to match reasonably well. For HgP and GEM, no distinct diurnal or seasonal patterns appeared in measured or modeled concentrations. Numerically, however, the model predictions for HgP were much higher than the measurements. For GEM, average modeled values were very close to average measured values; however, the fluctuations in the modeled time series were much greater than in the measurements – measured concentrations showed very little variability.

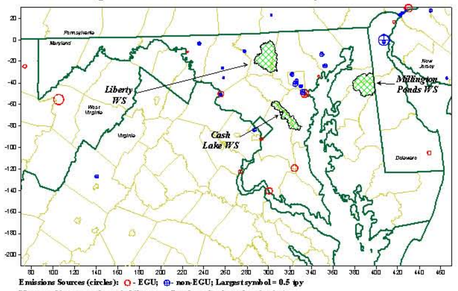
PPRP plans to continue the process of model evaluation and improvement, with a goal of updating inventory and meteorological inputs in order to conduct a more rigorous model evaluation. Work is also underway to develop a 10-year meteorological data set that can be used to evaluate long-term patterns based on changing weather conditions.

Acceptable concentration estimates are only the starting point for a model to be useful for evaluating mercury impacts. Wet and dry deposition, and ultimately loading to water bodies, are the end points that are needed. Measurements of dry deposition would fill an important data gap, and are indispensable in providing the remaining, missing link in model evaluation.

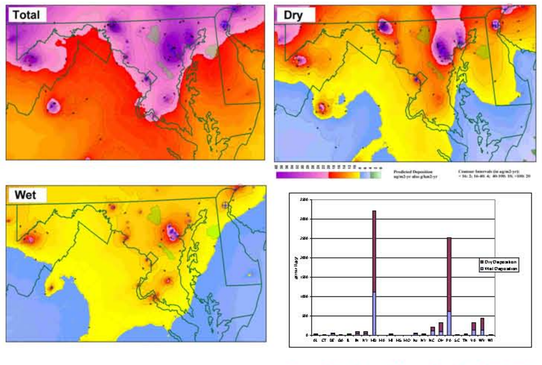
The Goalpost: Why Model?

A model capable of producing hourly concentration and deposition estimates, with the capability of determining source contributions to the deposition flux, is a useful tool in evaluating mercury impacts to Maryland's lakes and water bodies, and in evaluating alternative ways of achieving water quality goals. A study recently completed by PPRP used the CALPUFF model to estimate airborne mercury loading to several water bodies in different areas of the State, and to identify the relative contributions to mercury loading from specific anthropogenic sources as well as from the global pool. The plots shown below illustrate this application of the model. Instruments that are currently used to measure speciated mercury concentrations in air are not capable of producing a complete time series of RGM and HgP, producing a gap of approximately one hour every two hours. A model capable of producing a complete time series is useful in evaluating the impact of these time gaps, and PPRP has work underway to examine this impact.

Location of Hg Sources and Watersheds within Maryland



Model Predicted Deposition Contours



Source Contributions to Mercury Deposition Within Liberty Reservoir Watershed